Alkali-metal intercalated bilayer graphene studied by ARPES

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論 文 内 容 要 旨

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論 文 要 旨

1. Introduction

Graphite intercalation compounds (GICs), composed of alternating graphene and metal layers, have become a target of intense research due to the observation of superconductivity at temperatures as high as 11.5 K in C_6Ca. Recently, it has become possible to fabricate bilayer graphene intercalation compounds composed of two graphene layers with a metal layer sandwiched between them. In this thesis, we report on novel bilayer graphene intercalation compounds C_8KC_8 and C_8RbC_8, and the metal-covered bilayer graphene intercalation compound $Cs_xC_8CsC_8$. These materials present an excellent opportunity to investigate the mechanism of superconductivity in GICs, and the potential for synthesizing a thin film analog to the traditional bulk system. Their electronic structures are investigated using angle-resolved photoemission spectroscopy (ARPES), and the potential for superconductivity similar to GICs is discussed.

2. Fabrication of Alkali Atom Intercalated Bilayer Graphene

Bilayer graphene was fabricated by annealing a 6H-SiC(0001) single crystal at 1500-1600°C under a 1.1 MPa argon atmosphere. Samples were characterized by low-energy electron diffraction (LEED), atomic force microscopy (AFM), and ARPES to determine the layer number and terrace size. By LEED, a (1x1) spot due to graphene was observed, in addition to a (1x1) spot originating from the SiC substrate, and a $(6\sqrt{3}x6\sqrt{3})R30°$ pattern corresponding to the carbon buffer layer between the substrate and first graphene sheet. K, Rb, or Cs ions were deposited at base pressures better than 3×10^{-10} Torr. During deposition bilayer graphene samples were held at 90K in the case of K and Rb, and room temperature in the case of Cs. After K and Rb deposition, a clear (2x2) pattern was observed for sample surfaces, consistent with the creation of an intercalated layer similar to bulk alkali-metal GICs. In Cs case, a triangular shape corresponding to a nearly commensurate (2x2)* structure was obserserved in addition to the commensurate (2x2) pattern. This is consistent with the Cs surface phase observed from Cs deposited on bulk graphite at low temperature. This suggests that Cs-intercalated bilayer graphene with a Cs overlayer, $Cs_xC_8CsC_8$, was synthesized.

3. Electronic Structure of K-Intercalated Bilayer Graphene, C_8KC_8

The electronic structure of C_8KC_8 was investigated with ARPES. A rigid band shift of σ, π, and π* bands was observed, which can be attributed to charge transfer from the intercalated K layer. We observe folding of the π and π* bands due to the regular potential of the intercalated K atoms. At the Fermi level a large triangular surface attributed to the π* bands is seen, which is also folded by the potential of the K superstructure. From the area of the observed Fermi surface, the occupancy is estimated to be 0.7 e-/ unit cell. Since the valency of the K atoms is 1 e-, the remaining 0.3 e- is inferred to occupy the interlayer band.

4. Electronic Structure of Rb-Intercalated Bilayer Graphene, C_8RbC_8

In C_8RbC_8 a clear (2x2) superstructure exists, which provides good evidence for the strong ordering of the intercalated atoms. A total charge of 0.93 e- was estimated from the Fermi surface of C_8RbC_8, consistent with the expected 1 e- valence charge of the intercalated Rb atoms. At the Γ point a free-electron-like state is observed,

consistent with the interlayer band in bulk GICs. The interlayer band occupancy is 0.53 e- in C_8RbC_8. This represents the first observation of the interlayer band in alkali-metal intercalated bilayer graphene using ARPES. Based on the importance of this electronic feature to superconductivity in bulk GICs, we suggest that superconductivity may be possible in C_8RbC_8 at low temperatures.

A *kink* structure was found in the π* bands of C_8RbC_8 near the Fermi level. This feature is consistent with strong electron-phonon coupling, as seen in bulk GICs. Based on the dispersion of the kink structure, self-energy analysis was performed at several wave vectors around the K point. Electron-phonon coupling (λ) was found to be both strong and anisotropic, ranging from $\lambda = 0.16$ to $\lambda = 0.41$. This strong electron-phonon interaction can be attributed to in-plane optical carbon phonons near 170 meV, as well as out-of plane carbon modes, or intercalant-derived modes, near 90 meV. The observed coupling is signficiantly strong than that of metal-absorbed monolayer graphene, suggesting that the electron-phonon coupling strength is enhanced by the strong crystal order of the intercalated atom layer in bilayer graphene. This dependence of coupling on the crystal structure confirms the importance of stacking and dopant atom order in determining electron-phonon coupling, and indicates that the structure of dopant atoms must be carefully considered in future studies of superconductivity in graphene.

5. Electronic Structure of Cs-Intercalated Bilayer Graphene with a Cs Overlayer, Cs_x-C_8CsC_8

This sample exhibited band folding due to the (2x2) periodic potential in $Cs_xC_8CsC_8$, as well as heavy electron doping, consistent with DFT calculations for C_8CsC_8 doped by additional charge transfer from the Cs overlayer. A free-electron-like interlayer band was found at the Γ point, in agreement with DFT calculations. Based on the Fermi surface area, the π* bands of $Cs_xC_8CsC_8$ have an estimated electron occupancy of 1.04 e-/ unit cell, while the interlayer band has an occupancy of 0.46 e-/ unit cell. This is substantially more than for C_8KC_8 or C_8RbC_8, which we attribute to the presence of the Cs overlayer. A strong kink of the π* bands was found near E_F, similar to that of C_8RbC_8. Based on the dispersion of the kink, the self-energy and electron-phonon coupling constant were estimated. The average coupling of $Cs_xC_8CsC_8$ is $\lambda = 0.49$, which is much larger than that in Rb-intercalated bilayer graphene and doped monolayer. This enhancement can be attributed to the regular ordering of the intercalated Cs atoms, and the additional electron doping from Cs overlayer to the π* bands, which creates conditions favorable to strong electron-phonon coupling.

6. Summary

I have fabricated K- and Rb-intercalated bilayer graphene, as well as Cs-intercalated bilayer graphene with a Cs overlayer, and elucidated the electronic structure of these samples using high-resolution ARPES. I observe large electron doping of the π bands by the intercalated metals. In C_8RbC_8 and $Cs_xC_8CsC_8$ large electron-phonon coupling and an occupied interlayer band are observed, features strongly correlated with superconductivity in GICs. As these structures are not observed in doped monolayer graphene I attribute them to strong ordering of the intercalated atoms, facilitated by intercalation into the graphene bilayer. Based on these results, I predict that superconductivity may be possible in these two compounds, and suggest that the intercalation and ordering of dopants must be carefully considered in order to achieve superconductivity in monolayer graphene.

論文審査の結果の要旨

グラファイトの層間にアルカリ金属等を挿入したグラファイト層間化合物(GIC)は、挿入原子の種類によって多彩な物性を示す。本研究では、GIC を極限まで薄くした２層グラフェン層間化合物の電子状態を、高分解能角度分解光電子分光(ARPES)によって研究した。

本論文では、Ar ガス雰囲気中で SiC を 1600°C まで加熱することで、大面積のテラスを持つ高品質２層グラフェンを作成した。超高真空下においてこの試料にアルカリ金属原子(K, Rb, Cs)を蒸着することで、アルカリ原子が規則的に挿入された２層グラフェン層間化合物(C_8AC_8; A = K, Rb, Cs)を作成した。低速電子線回折パターンがバルク GIC と同様の 2×2 超周期構造を示すことから、アルカリ原子が層間に規則的に挿入されていることを確認した。さらに、C_8CsC_8 においては、その表面に不整合な超周期構造をもつ Cs 層が形成されていることを見出した。作成した２層グラフェン層間化合物の電子構造を ARPES で決定し、C_8RbC_8 および $Cs_xC_8CsC_8$ においては、挿入原子の超周期ポテンシャルに起因したグラフェン由来のπ/π*バンドの折り返し構造の他に、バルク GIC において超伝導との関連が指摘されている層間電子バンドの観測に成功し、2 層グラフェン層間化合物における２次元超伝導の可能性について議論した。また、C_8RbC_8 および $Cs_xC_8CsC_8$ のπ*バンドに、電子格子相互作用の存在を示す折れ曲がり(キンク)構造を観測し、自己エネルギーの解析から、電子格子結合定数が強い波数依存性を持つことを明らかにした。この異方性の起源として、層間原子のフォノンまたは炭素原子の面直方向振動のフォノンの重要性を議論した。$Cs_xC_8CsC_8$ においては C_8RbC_8 よりも強い電子格子相互作用を観測し、その原因がグラフェン表面上の Cs 層からの電子ドープによるものと結論した。

これまで不可能と考えられてきた２層グラフェン層間化合物の作成手法を独自に開発し、その電子状態を明らかにした本論文の成果は、提出者が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって，Kleeman Thomas James 氏提出の博士論文は，博士（理学）の学位論文として合格と認める。